Second Quarterly Progress Report

Covering the Period 1 October 1969-31 December 1969

DEVELOPMENT OF HIGH TEMPERATURE MATERIALS FOR SOLID PROPELLANT ROCKET NOZZLE APPLICATIONS

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INTRODUCTION

National Aeronautics and Space Administration research grant NGR NGR 34-002-108 was awarded to North Carolina State University for the development of materials for use in solid propellant rocket nozzles. The materials to be developed are to be resistant to both mechanical and chemical erosion as well as resistant to thermal shock. The materials should have the ability to provide the above properties particularly in the rocket nozzle throat area where the environment is most hostile.

This investigation proposed to develop a composite of refractory metals and/or graphite with a ceramic base. By the formulation of such a composite it is felt that the best properties of each type of material used will be imparted to the composite so that it will have the mechanical and chemical erosion as well as the thermal shock properties required for solid propellant rocket motor nozzles.

The first quarter of the research period was used for necessary preliminary work such as selection, acquisition, design, construction, installation of equipment; continuation of the literature survey; and the formulation of tests. This work is described in the First Quarterly Progress Report.

The second quarter of the research period has been devoted to the development of a hot pressing technique for composites of refractory metal carbides with graphite, and/or refractory metals. Zirconium carbide and hafnium carbide are the bases with graphite and/or tungsten used as additions. Techniques were developed so that acceptable densities of the various composites could be acquired.

DEVELOPMENT OF HOT PRESSING TECHNIQUE

General Comments

Hot pressing techniques for composites of zirconium carbide or hafnium carbide with graphite and/or tungsten - 3% rhenium alloy were developed during the second quarter of the research period. The materials listed below were fabricated:

1. ZrC
2. ZrC-Graphite
3. ZrC-W
4. ZrC-Graphite-W
5. HfC
6. HfC-Graphite
7. HfC-W
8. HfC-Graphite-W

Graphite was varied from 0 to 35.5 atomic percent in the ZrC-Graphite composites and from 0 to 25 atomic percent in the HfC-Graphite composites. Tungsten additions were 10 weight percent of the composite.

All specimens were hot pressed in 1/2 inch Poco HPD-1 grade graphite dies with a die pressure of 10,000 pounds per square inch. Tantalum die ram end shields were employed to retard sticking between the die ram and the sample. Temperatures up to 2400°C were obtained by induction heating. Temperature measurements were made by optical pyrometry.

Hot pressing technique evaluation was made on the basis of density measurements and microhardness measurements. (These properties are not necessarily to be considered as a basis for selection of materials for application. They are, however, to be used in future investigations

to help correlate the applicability of materials to their physical properties and method of fabrication.) Density measurements were made in accordance with ASTM Designation B311-58 entitled "Standard Method of Test for Denisty of Cemented Carbides." Microhardness measurements were made with a Knoop microhardness tester using a 100 gram load.

Raw materials were -325 mesh reactor grade hafnium carbide and zirconium carbide supplied by Wah Chang, -325 mesh powder graphite supplied by Poco Graphite, and 0.005 inch diameter tungsten -3% rhenium wire supplied by General Electric. Certified chemical analysis of the hafnium carbide and zirconium carbide are listed in Tables 1 and 2. In general, the major metallic impurities are niobium and tantalum. Nitrogen and oxygen are the major non-metallic impurities. An excess of 580 parts per million free carbon is reported for zirconium carbide and a similar level is expected but not reported for the hafnium carbide.

A certified chemical analysis of the graphite used was not given but Poco indicated the graphite to have only 5 parts per million impurities. No analysis was given by General Electric for their tungsten -3% rhenium alloy lamp filament wire used in this investigation.

During hot pressing an extensiometer was employed to measure die displacements. Classical densification would show a relatively rapid and nonlinear contraction of the hot pressed specimen until a certain density which is controlled by firing temperature and die pressure was obtained. At this point, the displacement vs time curve would be expected to level and show little or no subsequent contraction. This approach was used to determine the maximum densities which could be obtained for each given composition with respect to firing times and temperatures. As will be discussed later it was found in most cases

that for a given die pressure firing temperature, and composition, density did not vary appreciably as a function of firing time after sufficient time had elapsed for the displacement vs time curve to level.

ZrC and ZrC Based Composites

Zirconium carbide and composites of ZrC, graphite, and tungsten were hot pressed under pressures of 10,000 pounds per square inch in the temperature range of 1950-2375°C. Densities were obtained from approximately 87-97 percent of theoretical density. Because of the technique described above all densities can be related to composition and firing temperature.

Initially 5 gram samples of 100% ZrC were hot pressed. Figure 5 shows a plot of density vs firing temperature. In all cases the samples were fired until the die displacement vs firing time curves leveled off. The densities range from 6.10 grams per cubic centimeter at 1950°C to 6.50 grams per cubic centimeter at 2250°C. At a temperature of 2150°C several samples were hot pressed for times of 30 minutes to 1.5 hours. The densities obtained varied from 6.22 to 6.27. Figure 6 shows the die displacement vs firing time curves for two samples fired for 30 minutes and one sample fired for 1.5 hours. It may be noted that 30 minutes is just beyond the knee of the curve while 1.5 hours is well past the knee of the curve. It may be noted, however, that the die displacements remain essentially the same. This behavior tends to substantiate past experience and allows the use of the technique for determination of necessary firing times for maximum densities at specific firing temperatures of other compositions.

The binary phase diagram of carbon and zirconium shown in Figure 4 shows a eutectic composition of ZrC and carbon at 71.2 atomic percent

zirconium carbide and 28.8 atomic percent carbon. It is felt that this composition will represent an upper limit of carbon composition for the composites to be developed. For hot pressing technique evaluation, however, composition with carbon above and below this composition were hot pressed in the vacinity of 2150°F. The eutectic composition at this temperature yielded a density of 6.35 grams per cubic centimeter. The 85.6 atomic percent ZrC-14.4 atomic percent C composition yielded 6.38 grams per cubic centimeter and the 64.5 atomic percent ZrC-35.5 atomic percent C composition yielded a density of 6.25 grams per cubic centimeter. All these densities represent approximately 96.1 percent of theoretical density for each composition.

Densities of 6.75 grams per cubic centimeter were obtained from composites of 90 weight percent ZrC and 10 weight percent tungsten wire hot pressed at 2200°C. This composition is discussed in detail in a later section of this report.

Ternary composites of ZrC, C, and W are the composites of interest to this investigation. For hot pressing technique only composites of eutectic ZrC and carbon with 10 weight percent tungsten were fabricated. Densities ranged from 6.65 to 6.75 in the firing temperature range of 2150 to 2250°C. Determination of percent of theoretical density was not attempted because of loss of a small amount of ZrC and C powder during loading and outgassing the sample and the die. The densities are, however, believed to be in the range of 94-97 percent of theoretical density.

The general appearance of all zirconium carbide and zirconium carbide based composites samples was acceptable. Isolated cases of lamination cracking was observed but no correlation could be made

between the cracking and the hot pressing parameters of composition, firing temperature, or firing time. No cracking was observed in the vacinity of the tungsten wires and the matrix interfaces. A reaction zone between the matrix and the reaction zone was detected and this is the subject of a later section of this report.

Table 3 lists the compositions, firing temperatures, firing times, densities, and percentage of theoretical density of the various groups of materials which were fabricated. The information obtained from the above work will be used in the next two quarters of the research period to produce samples for oxidation and thermal shock testing. Carbon will be increased in 5 atomic percent increments from 0 to 25 atomic percent in compositions with no tungsten and samples with 10 weight percent tungsten. Duplications of each composition will be produced with high and low densities. The most satisfactory compositions will consequently be selected for further testing as a material for application.

HfC and HfC Based Composites

Samples of 100% HfC were pressed in the vacinity of 2150°C and densities of 11.68 grams per cubic centimeters on 92 percent of theoretical density. Subsequently samples of 25 atomic percent C and 75 atomic percent hafnium carbide and samples of 95 weight percent hafnium carbide and 5 weight percent tungsten were hot pressed. Their densities and hot processing parameteris are listed in Table 4. In general, densification was acceptable. Firing time was determined by observation of the die displacement vs firing time curves as was discussed previously.

Composites of 25 atomic percent C and 75 atomic percent hafnium carbide with 5 weight percent tungsten deviated from previous behavior. Figure 7 shows die displacement vs firing time curves for 100% HfC, 75 atomic percent HfC -25 atomic percent C, 95 weight percent HfC -5 weight percent tungsten, and 75 atomic percent HfC -25 atomic percent C with 5 weight percent tungsten composites. The latter composites do not show the expected behavior. The die displacement rises an insignificant amount and essentially remains level. This indicates that densification does not occur. The carbon content was adjusted to 12.5 atomic percent and the same behavior was observed. The densities for these listed in Table 4 are very low. The samples upon inspection are very soft and powder-like.

Because this phenomenon was observed late in the quarter no explanation is offered at this time. Investigation will continue in an attempt to explain the phenomenon, but it appears that this type of composite will not be applicable.

The hafnium carbide-graphite composites and hafnium carbide-tungsten composites do, however, show promise. The carbon composition will be varied in 5 atomic percent steps from 0 to 25 atomic percent carbon. These and samples containing 95 weight percent HfC -5 weight percent tungsten wire will be tested for thermal shock and oxidation resistance during the next quarter.

CARBON EMBRITTLEMENT OF TUNGSTEN

The use of tungsten wire as a component in a hot pressed composite containing other components which are composed in part or totally of carbon has been found to be hampered by the embrittlement of the tungsten by carbon. If the tungsten becomes embrittled, its role as an agent to impart improved thermal shock resistance to the composite is probably retarded.

The carbon-tungsten binary phase diagram (Figure 3) shows no solid solubility of carbon in tungsten. In the tungsten rich side of the diagram a two phase region of tungsten and variable composition W_2C exists in our hot pressing temperature range. On the carbon rich side and in the same temperature range, a two phase region of carbon and the same variable composition W_2C exists. If allowed to cool to 1215°C on the tungsten rich side or to 1325°C on the carbon rich side under equilibrium conditions the stable tungsten monocarbide WC will form.

The hardening and embrittlement of tungsten is attributed to the diffusion of carbon into interstitial sites in the tungsten body centered cubic crystal structure. It has been found by others that the addition of 3 percent rhenium to tungsten tends to retard embrittlement by retarding the diffusion of carbon into the interstitial sites. For this reason a tungsten -3% rhenium alloy was selected as the refractory metal component of the composites to be developed.

Initial investigation of this embrittling effect has been limited to composites of tungsten -3% rhenium wire, zirconium carbide and graphite. Composites of 100% zirconium carbide and tungsten -3% rhenium

wire and 71.2 atomic percent zirconium carbide -28.2 atomic percent graphite and tungsten -3% rhenium wire were hot pressed in the range of 2200-2300°C and 10,000 psi for various lengths of time. The relative amount of embrittlement was measured by microhardness testing.

The tungsten -3% rhenium wire as received had a Knoop Hardness Number in the 1600-1700 range. The wire when hot pressed in 100 atomic percent zirconium carbide at 2200°C for 30 minutes with a die pressure of 10,000 psi varied in Knoop Hardness Numbers of 1600 in the center of the wire to approximately 2400 near the outside of the wire. Free energy data for zirconium carbide and tungsten carbide does not predict the reaction

$$ZrC + W \rightarrow Zr + WC$$

or

$$ZrC + 2W \rightarrow Zr + W_2C$$

because ZrC is the more thermodynamically stable of the three carbides. The binary phase diagrams for zirconium and carbon (Figure 4) does however show a variable composition for ZrC which would allow the release of approximately 5 atomic percent carbon in the hot pressing temperature range of 2200-2300°C. Furthermore, the analysis of the zirconium carbide listed in Table 1 shows 580 pasts per million free carbon in the bulk. This, however, is a relatively small amount and is probably insufficient to cause the observed behavior. The formation of tungsten carbide may then proceed by either of the two following routes:

$$ZrC \rightarrow Zr_{1-x}C + XC$$

$$C + W \rightarrow WC$$

or

$$C + W \rightarrow W_2C$$

With this in mind, an examination of Figure 1 (which shows a tungsten -3% rhenium wire hot pressed in 100 atomic percent zirconium carbide) reveals a fine grained shell around the tungsten wire. This shell is probably W_2C and/or WC which was found by the free carbon which diffused into the outer portion of the wire. The Knoop Hardness number of this shell is approximately 3,500.

This behavior can explain the higher hardness near the surface of the wire. It should be noted that the bond between the sheel and the wire appears to be tenacious and that the fine grains mesh closely with the larger grains of the matrix. This arrangement is desirable if the tungsten wires are to strengthen the matrix and impart increased thermal shock resistance.

Figure 2 shows a tungsten -3% rhenium wire hot pressed in a 71.2 atomic percent zirconium carbide -28.8 atomic percent graphite matrix which was hot pressed at 2200°C for 30 minutes with a die pressure of 10,000 psi. The shell may again be noted and in this instance it completely surrounds the wire. The addition of 28.8 atomic percent graphite raised the hardness in the center of the wire from a Knoop Hardness Number of 2000 to approximately 7500 on the outside. This increase in hardness is of course due to the increase in the amount of available carbon. The Knoop hardness number of the shell is again 3,500.

The composition 71.2 atomic percent zirconium carbide -28.8 atomic percent graphite is a eutectic composition and represents an upper boundary carbon composition for the composites to be developed.

Because the length of time at temperature is determined by the rate of densification as discussed previously, 30 minutes at temperature

appears to be a lower time limit for good densification. This length of time is adequate for the above processes to occur. Longer lengths of time do not appear to alter the properties of the tungsten at the interface between the tungsten and the matrix. Thermal shock testing to be performed in the next quarter of the research period of compositions between 0 and 28.2 atomic percent graphite and 100 and 71.2 atomic percent ZrC should reveal the most desirable compositions from this standpoint.

Similar behavior is expected of hafnium carbide-graphite-tungsten composites because of the similarity between hafnium carbide and zirconium carbide. The behavior will be characterized in the next quarterly progress report.

Table 1

Chemical Analysis of Raw Material-ZrC

Analysis in PPM	
Al	<25
B	0.8
C	10,0%
Cb	<100
Cd	<0.3
Co	<5
Cr	15
Cu	<25
Fe	<50
Hf	166
Mg	<10
Mn	<10
Mo	<10
N	245
Ni	25
O	230
Pb	<5
Si	<40
Sn	<10
Ta	<200
Ti	<20
V	10
W	100
Zn	<50

Table 2

Chemical Analysis of Raw Material-HfC

	Analysis in PPM
Al	<25
B	0.5
C	6.15%
Cb	<100
Cd	<1
Co	<5
Cr	<10
Cu	<40
Fe	<50
Mg	<10
Mn	<10
Mo	<10
N	100
Ni	<10
O	260
Pb	<5
Si	<40
Sn	<10
Ta	<200
Ti	0.5-0.8%
V	50
W	<20
Zr	1.8%

Table 3

ZrC and ZrC Composite Data

Composition (atomic %)	Firing Temperature (°C)	Firing Time (Min.)	Density (gm/cm^2)
100% ZrC	1950°C	30	6-10
100% ZrC	2150°C	30-90	6.22-6.27
100% ZrC	2200°C	40	6.45
100% ZrC	2250°C	30	6.51
71.2% ZrC 28.8% C	2200°C	75	6.35
85.6% ZrC 14.4% C	2250°C	60	6.38
64.5% ZrC 35.5% C	2200°C	60	6.25
71.2% ZrC 28.8% C with 5 wt.pct. tungsten	2200°C	30	6.70
95 wt.pct. ZrC 5 wt.pct. W	2200°C	30	6.75

Table 4

HfC and HfC Based Composite Data

Composition (atomic %)	Firing Temperature (°C)	Firing Time (Min.)	Density (gr/cm^3)
100% HfC	2200°C	45	11.70
75% HfC 25% C	2200°C	40	10.50
75% HfC 25% C with 5 wt.pct. tungsten	2000-2375°C	30-180	All samples too porous to measure density

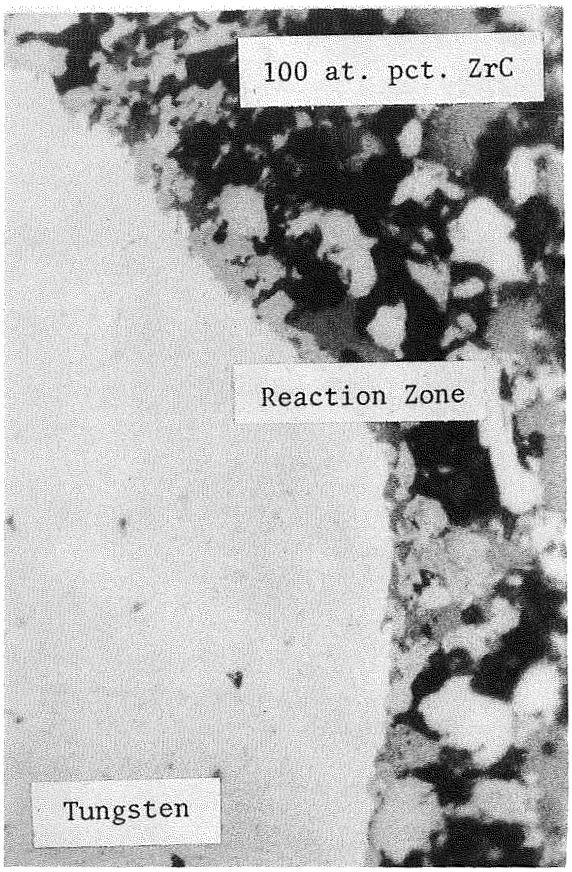

Fig. 1. Photomicrograph showing ZrC-W composite with a partial reaction zone between ZrC and tungsten after hot pressing. 150X

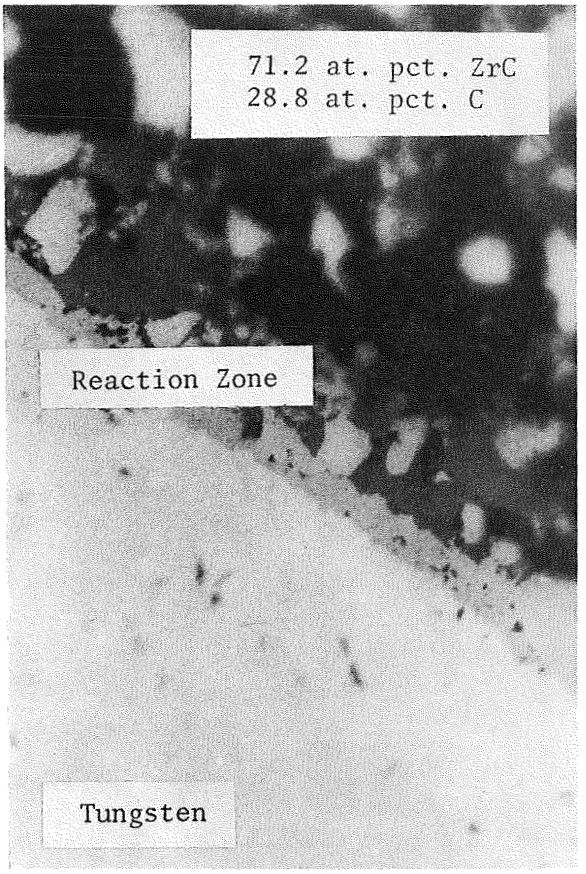

Fig. 2. Photomicrograph showing ZrC-C-W composite with a complete reaction zone between ZrC-C matrix and tungsten after hot pressing. 150X

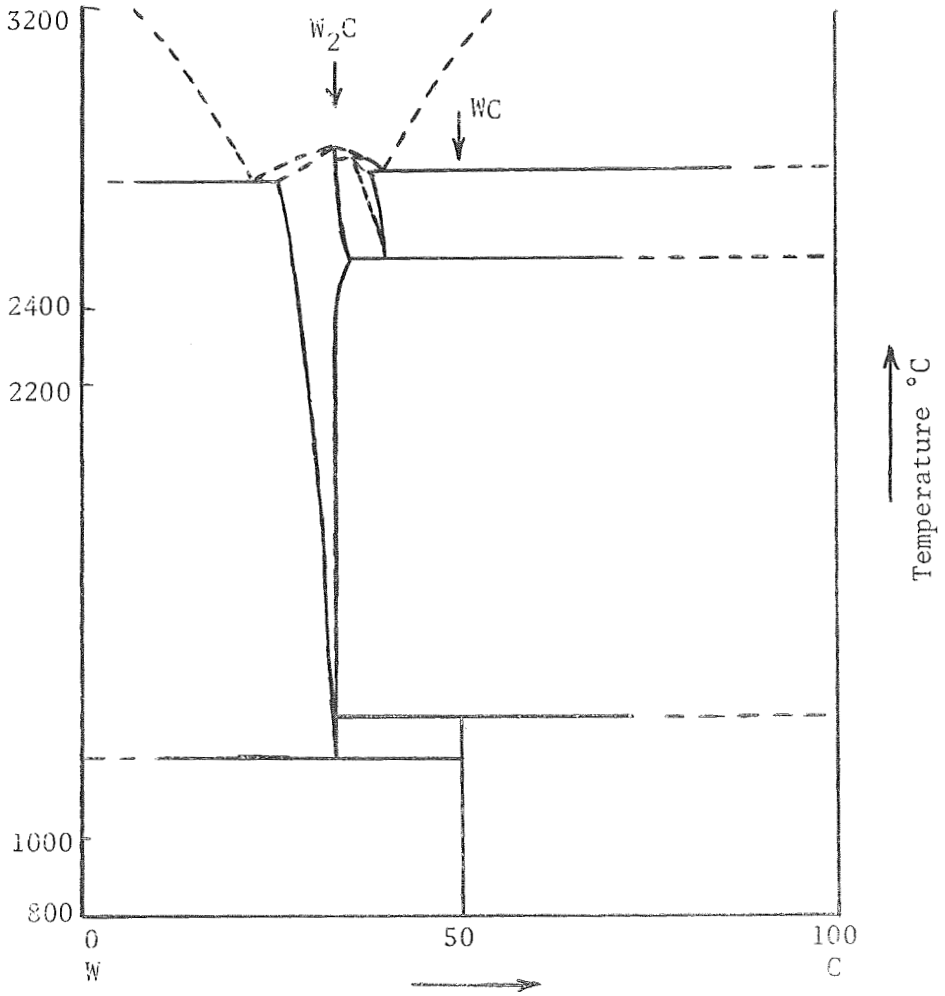

Figure 3. Carbon-Tungsten Binary Phase Diagram. (After R. P. Elliott, Constitution of Binary Alloys)

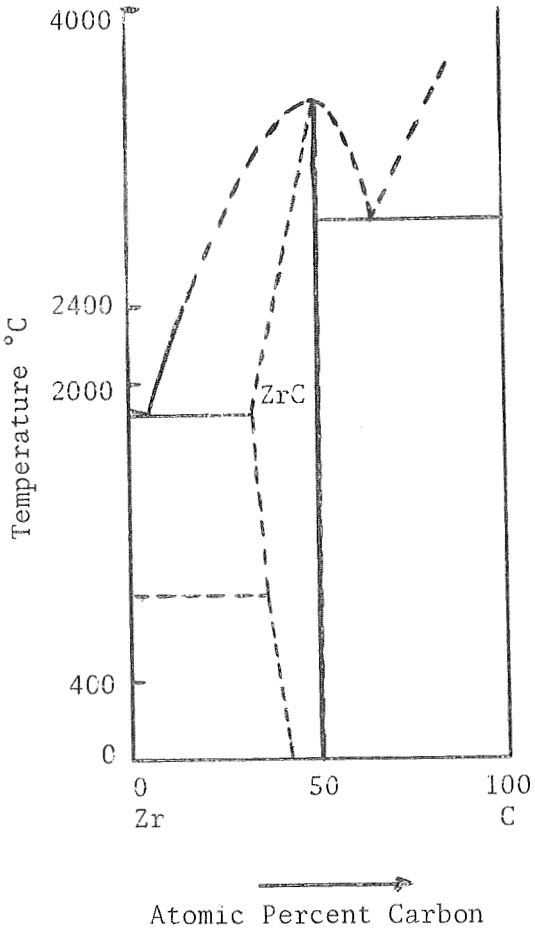

Figure 4. Carbon-Zirconium Binary Phase Diagram. (After R. P. Elliott, Constitution of Binary Alloys)

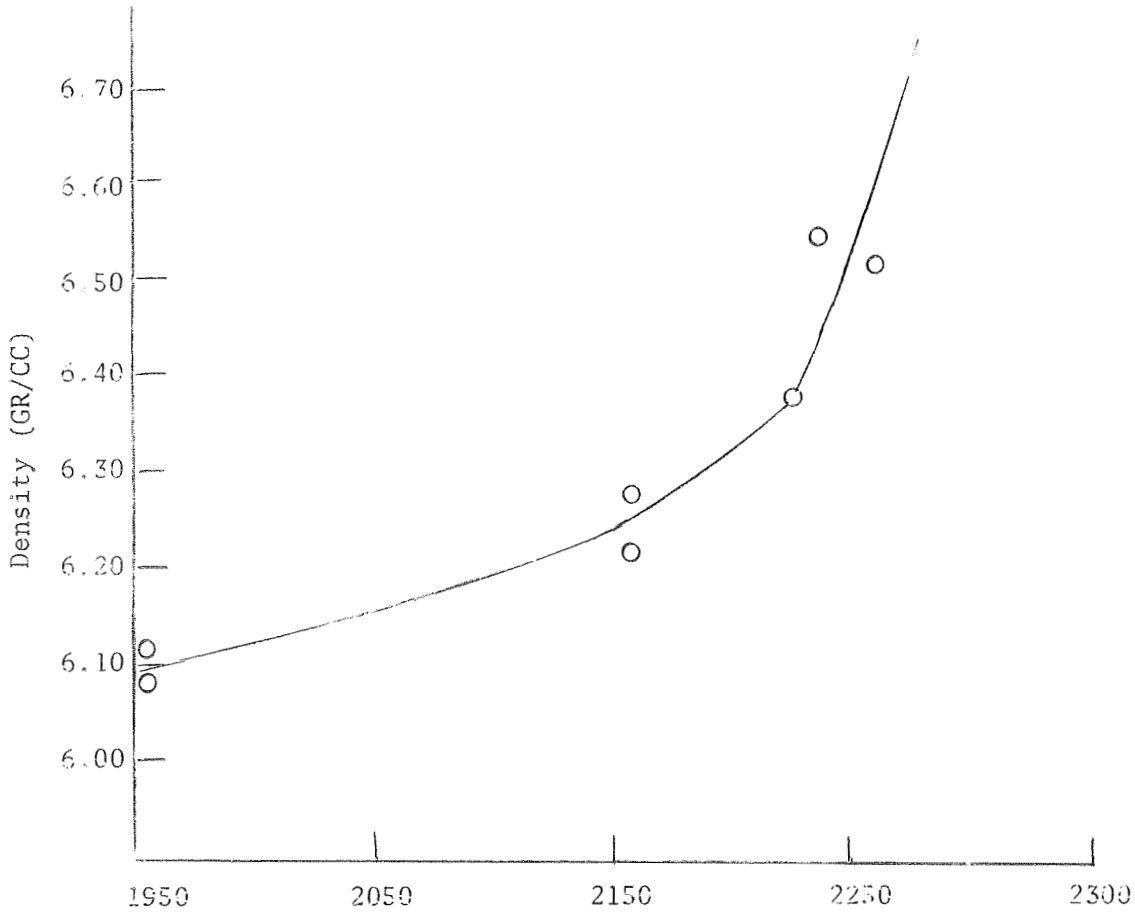

Figure 5. Density vs Firing Temperature for 100% ZrC

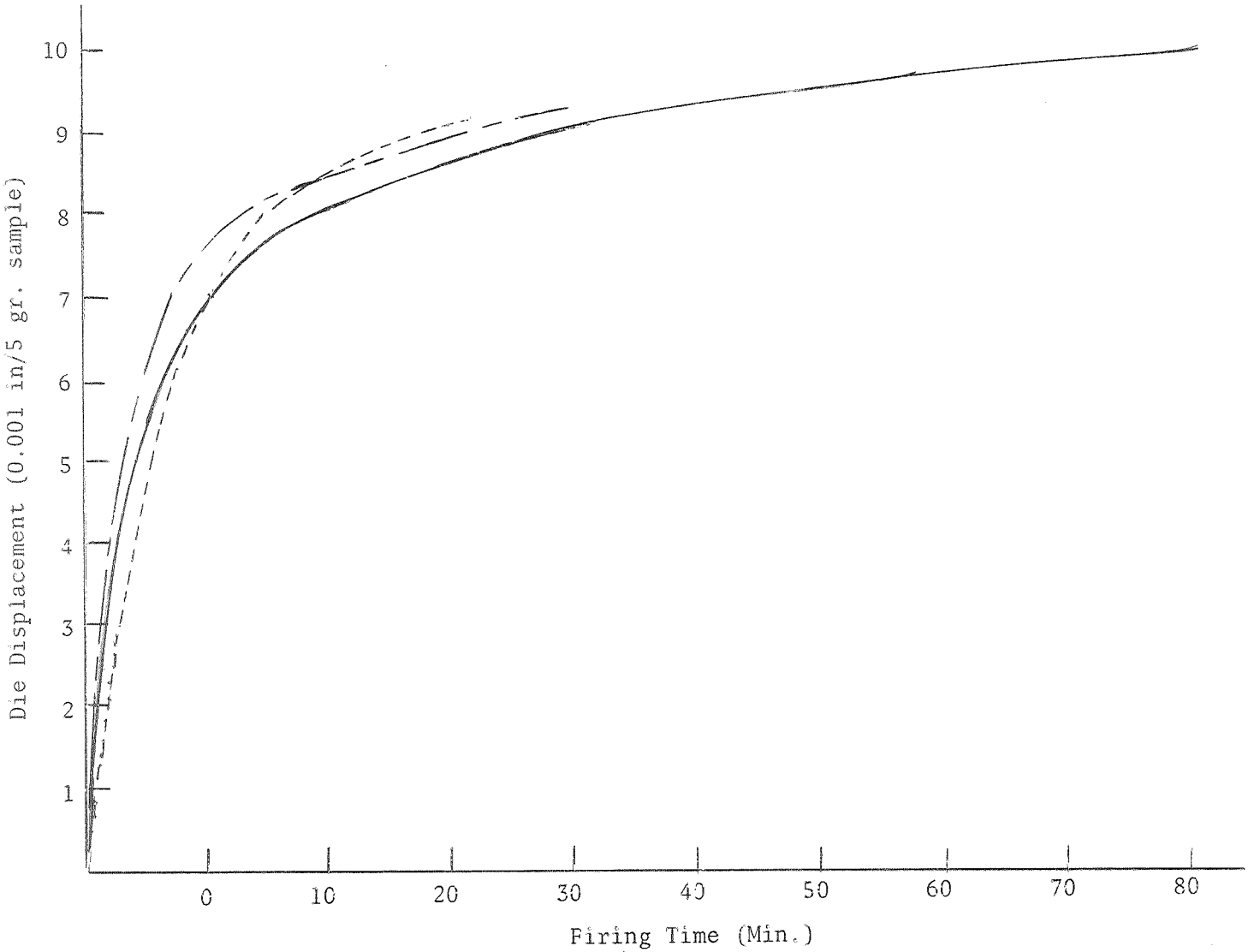

Figure 6. Die Displacement vs Firing Time for 100% ZrC Hot Pressed at 2150°C

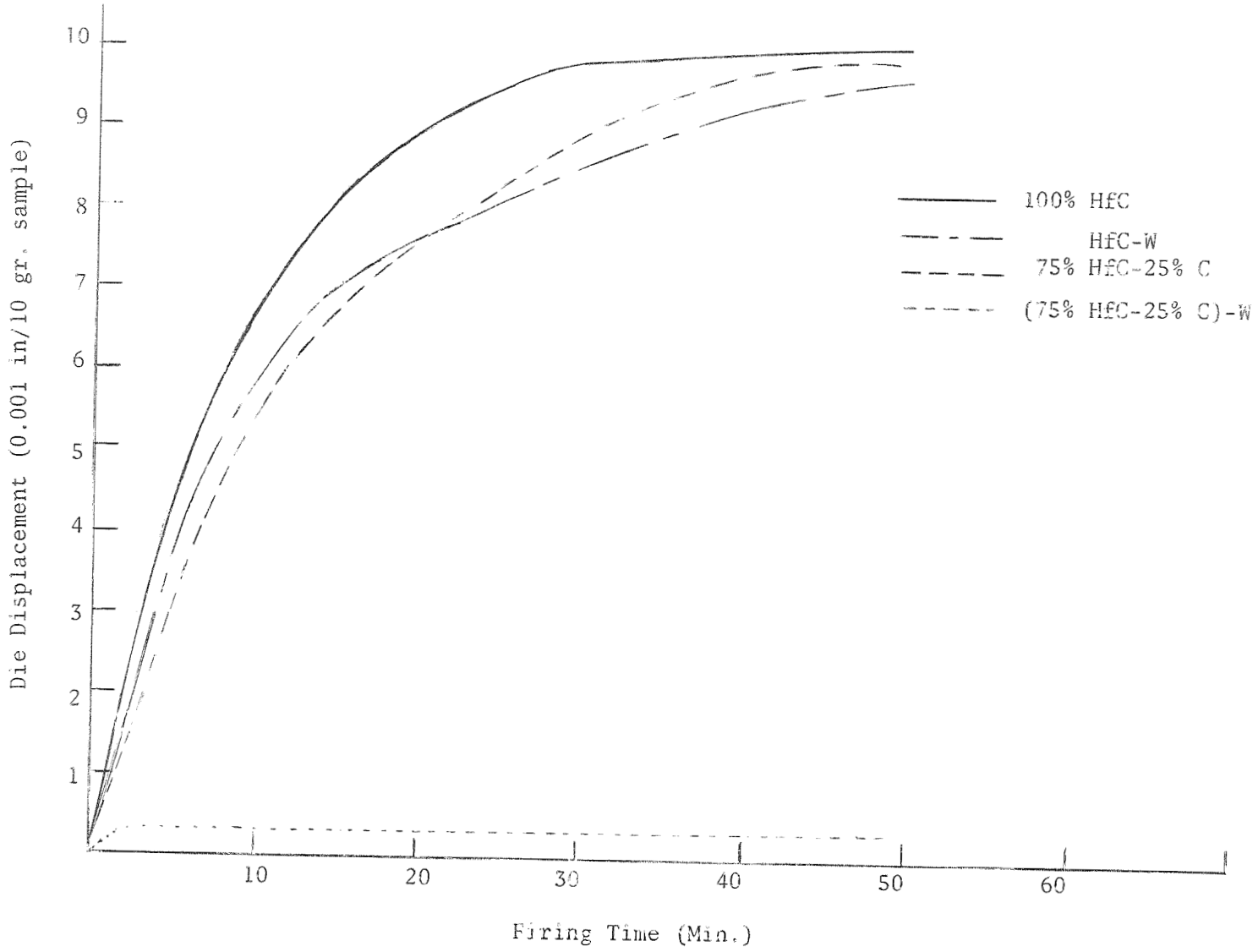

Figure 7. Die Displacement vs Firing Time for HfC Based Materials Hot Pressed in the Vacinity of 2150°C